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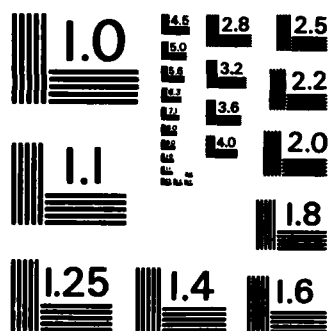
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TECHNICAL REPORT # 14

Microstructures Built from Electroactive Polymers:

Toward a Macromolecular Electronics

by

Royce W. Murray, Principal Investigator

Department of Chemistry

University of North Carolina

Chapel Hill, North Carolina 27514

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22. ABSTRACT (Continue on reverse side if necessary and identify by block number) <u>Summary.</u> Electrodes can be coated with electrochemically reactive polymers in several microstructural formats called sandwich, array, bilayer, microelectrode, and ion gate electrodes. These microstructures can be used to study the transport of ions through in the polymers as a function of the polymer oxidation state, which is essential to understanding the conductivity properties of these new chemical materials. The microstructures also exhibit potentially useful electrical and optical responses, including current rectification, charge storage and amplification, electron hole pair separation, and gates for ion flow.		

## MICROSTRUCTURES BUILT FROM ELECTROACTIVE POLYMERS:

### TOWARDS A MACROMOLECULAR ELECTRONICS?

Christopher E. D. Chidsey and Royce W. Murray

Miniaturization has value in many areas ranging from basic science to technology. In the study of films of electron transfer active polymers, miniaturization has several quite important benefits, a significant one of which is shortening the distances over which ions and electrons must move for the electrical, ionic and other chemical properties of these polymers to be measured. This article will first discuss how fundamental studies of these relatively new, conductive materials can be aided by working with small structures, and will then introduce some possible technological applications of microstructures built from these polymers. The microstructures have already achieved impressively small dimensions, ranging from 5 nm to 10  $\mu$ m, but those that have been made are neither numerous nor highly sophisticated. They should be viewed as pioneer structures which may in the future evolve into useful devices under the heading: "macromolecular electronics".

Let us begin with a few words about electroactive polymers, which are themselves relatively new and vigorously researched, materials. Electroactive polymers fall into three, still-growing families (1-4); see Fig. 1. Common features of electroactive polymers are their semirigid mechanical properties, the ability to pass electrical current in some manner, and the ability to be oxidized or reduced by electrolysis. They are ordinarily used as films in contact with electrodes, which serve both as connectors for the electron flow

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Christopher E. D. Chidsey and Royce W. Murray

C.E.D. Chidsey is a member of the technical staff of AT&T Bell Laboratories, Murray Hill, NJ 07974. At the time this article was written he was at the Department of Chemistry, University of North Carolina, Chapel Hill, NC 27515, where R. W. Murray is Kenan Professor and Department Chairman.

Summary. Electrochemically reactive polymers can be coated on electrodes in several microstructural formats called sandwich, bilayer, array, microelectrode, and ion gate electrodes. These microstructures can be used to study fundamental properties of electron and ion transport in the polymers and have potentially useful electrical responses.

Keywords: electrode, electronics, polymer, electron hopping, conductivity.

and provide the electrical potential driving force for the oxidation state changes.

The  $\pi$ -conjugated materials, poly-acetylene and poly-pyrrole being examples, have relatively delocalized electronic states, are electronically conducting, and are sometimes called "organic metals". The conductive states are made by oxidative or reductive "doping" with chemical reagents like oxygen (5), the halogens (6), arsenic pentafluoride (7), or electrochemically by partial oxidation or reduction in contact with an electrolyte solution (8,9). The other two families in Fig. 1, redox polymers (10-14) and ion exchange polymers loaded with electroactive ions (15-16), are localized state conductors and correspond to the  $\pi$ -conjugated materials, are less highly conducting. They conduct current by, respectively, electron self exchange (hopping) between neighbor redox sites and by physical diffusion of the electroactive ions.

The film-making step is an important aspect of successfully fabricating microstructures from electroactive polymers. Films have been formed in many ways (1,2), including casting from solutions of the polymer or of reactive monomers (typically organosilanes), grafting of redox sites onto already formed polymer films, ion exchanging into ion exchange polymer films, and electrochemical polymerization from monomer solutions. Electrochemical polymerization has been a particularly effective method for microstructuring, and the poly-pyrrole and poly-[Os(bpy)<sub>2</sub>(vpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> films of Fig. 1 are made in that way (8,10).

Electroactive polymer films are interesting to electrochemists because these chemicals can be used to store electrical charge or as catalysts in electrochemical reactions. Both uses require the presence of mobile ionic species (counterions) to maintain electroneutrality in the electroactive

polymer as it is oxidized or reduced. For example, during oxidation of a film of poly-[Os(bpy)<sub>2</sub>(vpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, additional anions will migrate into the film from a contacting electrolyte solution,



As another example, reducing the conducting, poly-cationic form of poly-pyrrole produces a more neutral material, and the excess anionic counterions egress into the solution. The necessity for such ion motion events has a strong bearing on the proper design of electroactive polymer microstructures.

Electroactive polymers have similarities with two classical components of electrochemistry; these are on the one hand dense, highly conducting metal electrodes, and on the other small, freely diffusing ions and molecules in electrolyte solutions. Somewhat like metallic electrodes, electroactive polymers can conduct electrons and have some mechanical rigidity — structures can be built from them, thin films can be formed and can act as mechanical barriers between phases, and small spots and strips of polymers can be made and retain their shape. But unlike solid metals and more like solutions, the interior of electroactive polymers have variable compositions and are dynamic matrices. Counterions move in them, as indicated above. Other species such as solvent molecules or other solutes may have significant long range mobility while redox groups like the ferrocene sites in poly-vinylferrocene (Fig. 1) may only move over a few nanometers before being restrained by the polymer backbone.

Clearly, understanding transport of electrons and ions through

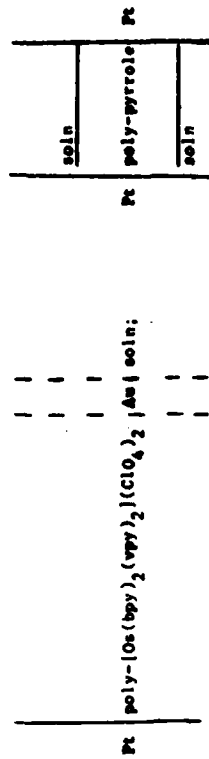
electroactive polymers is an important topic and has been both a significant part of polymer-coated electrode research and a source of impetus for the small

structures discussed in this article. We now turn to how these transport events and other fundamental characteristics of electroactive polymers have been studied with microstructured polymer electrodes.

#### MICROSTRUCTURES

The first microstructures of electroactive films were the "bilayer electrodes" (Fig. 2D and 2E) which are films of two different electroactive polymers, one atop the other (17). That development is only a few years old but has been followed by the development of several other microstructures as diagrammed in Fig. 2. The emphasis in such studies is not only on making microstructures whose electrical behaviors are interesting or potentially useful, but equally on using microstructures as tools to probe the fundamental properties of the constituent electroactive polymers and of their interfaces with one another.

**Sandwich Electrodes.** The sandwich electrode (Fig. 2A), in which a polymer film is sandwiched between two metallic conductors (18), is conceptually the simplest of the microstructures. The electrical conductivity of the polymer, and how it depends on the electrochemical (oxidation) state of the polymer, may be directly measured provided that the sandwich construction allows for supplying or removing the necessary counterions (see Reaction 1). In the case (10) of several hundred nanometer thick films of  $\text{poly}[\text{Os}(\text{bpy})_2(\text{vpy})_2](\text{ClO}_4)_2$  on Pt electrodes, counterion access was provided by using a porous (evaporated) Au film as the second electrode. In the case of 10  $\mu\text{m}$  films of poly-pyrrole on Pt, the second electrode was a solid Pt electrode brought into contact with the film by a sensitive micrometer (19). Unless the second Pt electrode is temporarily removed, counterion access becomes constrained to the edges of the film, which is less effective. These arrangements are shown schematically as



The electrochemical potentials of the two electrodes of either sandwich can be independently controlled with respect to a reference electrode immersed in the contacting electrolyte solution. Applying the same potential (relative to the reference electrode) to both electrodes of the sandwich fixes the oxidation state of the electroactive polymer. The current which then flows between the two contacting electrodes when their potentials are next made slightly different, say  $\Delta E = 5\text{mV}$ , gives the conductivity of the polymer at that oxidation state.

Fig. 3B shows how the conductivity of poly-pyrrole, measured by applying  $\Delta E$  between the electrodes of a sandwich electrode, varies with the polymer oxidation state. Poly-pyrrole when reduced is a poor conductor but when oxidized at potentials more positive than about  $-0.1\text{V}$  vs. SCE is a relatively good conductor (19,20). The cyclic voltammogram of Fig. 3A shows how the electrolysis current which flows into a poly-pyrrole film (on a simple Pt electrode) varies when the potential is cyclically scanned. Though the charging current at the scan rate used is obviously not thermodynamically reversible, it does give an indication of the capacity of the film to store charge. Comparing Figs. 3A and 3B, we see that the considerable oxidative charge which can be stored in poly-pyrrole at potentials more positive than  $-0.1\text{V}$  is not accompanied by further change in the conductivity. Understanding the molecular nature of this unusual oxidation remains an active research topic (19,21-23).

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Two additional observations for poly-pyrrole are, first, that the current flow through a film of oxidized polymer under a given  $\Delta E$  is the same whether it is dry or wetted with solvent as in Fig. 3B, and secondly, that the solvent-wetted polymer conducts ohmically up to at least  $\Delta E = 100\text{mV}$  (i.e., current is linear with  $\Delta E$  over that range). The ohmic behavior is seemingly straight forward evidence (19) that the electron flow through the poly-pyrrole is driven by a voltage gradient in the film between the two electrodes. This "ohmic" explanation is not unambiguous, however, if one considers the possible consequences of the counterions in the polymer moving appreciably under the influence of the voltage gradient. The counterions, if mobile, will tend to move to eliminate the electric field, and after a long enough time, will accumulate at the interfaces of the metallic electrodes. The applied  $\Delta E$ , now dropped in part at the two polymer/electrode interfaces, must be accompanied by some oxidation of the polymer at one electrode and reduction at the other. If this occurs, steady-state conduction becomes driven not by the full potential gradient, but instead by a concentration gradient of poly-pyrrole charge carriers. The "ohmic" experimental result for oxidized poly-pyrrole implies instead to both immobility of the counterions and the absence of redox charging due to the imposed bias. The answer to this apparent contradiction is not yet known.

Electron conduction in sandwich electrodes containing poly- $[\text{Os}(\text{bpy})_2(\text{vpy})_2](\text{ClO}_4)_2$  (10,24,25) is more completely understood. Fig. 4A plots the electrochemical capacity  $q$  of this polymer to store charge as a function of the electrode potential. This plot has the same appearance as a cyclic voltammogram of this polymer, and each of the peaks corresponds to a change of oxidation state. The peaks are centered at the polymer's standard

potentials, +0.72, -1.33 and -1.53V vs. SSCE (NaCl saturated SCE reference electrode). Reduction of the  $\text{Os(III)}$  state of the polymer to  $\text{Os(II)}$  is primarily a metal-centered reduction, whereas the next two reductions (to the  $\text{Os(I)}$  and  $\text{Os(0)}$  forms) are primarily centered on the two bipyridine ligands.

Applying a small  $\Delta E$  between the two electrodes of the poly $[\text{Os}(\text{bpy})_2(\text{vpy})_2](\text{ClO}_4)_2$  sandwich and varying their average potential relative to the SSCE produces a profile of conductivity as a function of oxidation state of the polymer film (Fig. 4B). The conductivity plot has features corresponding to each of the capacity peaks in Fig. 3A. That is, conduction occurs when the film is in a mixed-valent state. It is only then that electrons on reduced sites can hop to oxidized sites allowing electron conduction. This self-exchange process can be written:



The counterions migrate within the polymer to eliminate the applied field in the bulk of the polymer so that  $\Delta E$  is instead dropped at the two polymer/electrode interfaces. The driving force for electron hopping is the concentration gradient of reduced sites. This feature of steady state electrical conduction in electroactive polymers which contains mobile counterions has led to the term "redox conduction" (10). It is important to note that, while redox conductivity can be expressed in the same units as electrical conductivity (i.e.,  $\text{A/cm-V}$ ), redox conduction is driven by an electrochemical potential (e.g., concentration) gradient not simply an electric field.

In examining the electrical behavior of polymers like poly- $[\text{Os}(\text{bpy})_2(\text{vpy})_2](\text{ClO}_4)_2$  polymer using a transient technique (26), it is difficult to distinguish whether the electrical conductivity is controlled by



electron or by counterion mobility, since electrons and counterions are made to migrate concurrently throughout the polymer film as the electrochemical reaction proceeds. In the sandwich electrode on the other hand, the electron flow through the polymer is a steady state process in which the average polymer oxidation state has been fixed and net counterion migration has ceased, so that counterion motions are less capable of controlling the current. Thus, the sandwich microstructure allows a more direct measurement of electron mobility.

If now a larger  $\Delta E$  (say, 200mV), centered at  $\sim 0.73V$  vs SCE (the formal potential of the  $Os(III)/Os(II)$  couple) is applied across the poly- $[Os(bpy)_2(vpy)_2](ClO_4)_2$  sandwich, all of the polymer contacting one electrode becomes oxidized to the  $Os(III)$  state and all at the other reduced to  $Os(II)$ . Fig. 3A diagrams the steady-state concentration profile of  $Os(III)$  and  $Os(II)$  sites that develops across the sandwich. The current which flows is the largest that can be supported by the  $Os(III/II)$  mixed-valent state of the sandwich. This limiting current is given

$$i_{lim} = nFAD_{e(III/II)} C_T/d \quad (3)$$

where  $F$  is the Faraday,  $A$  the sandwich electrode area,  $D_{e(III/II)}$  the  $Os(III/II)$  electron diffusion constant,  $C_T$  the total concentration of  $Os$  sites (ca.  $1.4 M$ ), and  $d$  the film thickness.

The electron diffusion coefficient  $D_e$  is a quantity used to measure the rate of Reaction 2, i.e., the mobility of charge carriers in polymers like poly- $[Os(bpy)_2(vpy)_2](ClO_4)_2$  where conduction is driven by concentration gradients. The value of  $D_e$  corresponds to the mean squared displacement of the electron

per unit time and can be shown to be the ratio,  $\sigma/F$ , of redox conductivity to electrochemical capacity of the material (27).

Redox conductivity varies with electrochemical potential as is clearly seen by comparing Figs. 4A and 4B.  $D_e$  is approximately constant for each particular mixed-valent state, i.e., we can discuss  $D_{e(III/II)}$ ,  $D_{e(II/I)}$ , and  $D_{e(I/O)}$ . In Fig. 4B, the relative height of each conductivity peak reflects the relative mobility ( $D_e$ ) of the charge carriers associated with each change of polymer oxidation state. The electrons which reduce the  $Os(III)$  complex to the  $Os(II)$  complex are about 20 times less mobile than those that reduce the  $Os(II)$  complex to the  $Os(I)$  complex. Said in more molecular terms, the self exchange reaction rates differ for the  $Os(III)/Os(II)$ ,  $Os(II)/Os(I)$ , and  $Os(I)/Os(O)$  couples, and this gives rise to the different  $D_e$  and redox conductivities shown in Fig. 4B.

Comparing Figs. 3B and 4B, which are normalized for film thickness and electrode area, the electron conductivities of poly- $[Os(bpy)_2(vpy)_2](ClO_4)_2$  films are seen to be smaller than that for poly-pyrrole even for the most conductive mixed-valent state,  $Os(II/O)$ . This reflects the difference in electron mobility in a delocalized band material like poly-pyrrole and in a material where the electron faces a significant kinetic barrier between each pair of adjacent monomer sites.

We should mention an important recent variant (28) of the poly- $[Os(bpy)_2(vpy)_2](ClO_4)_2$  sandwich electrode experiment, in which the electrode is not immersed in an electrolyte solution, but is instead bathed in a solvent containing no electrolyte (such as toluene or pentane), or in a gaseous medium like  $H_2$  with or without solvent vapor, or under vacuum. If we now attempt to generate the situation of Fig. 3A by applying a potential  $\Delta E = 200$  mV across

the electrodes of the sandwich, no current will flow. To attain the steady state concentration gradients of Fig. 5A, half of the film became oxidized to the poly-[Os(hpy)<sub>2</sub>(vpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> state. In an electrolyte-less or dry medium, the extra ClO<sub>4</sub><sup>-</sup> counterions necessary to accomplish this oxidation while maintaining overall charge balance in the film, are simply not available. In other words, there is a restricted ion budget available, and conduction will occur only under circumstances not violating it.

Bottom conduction can be obtained in the dry sandwich within the ion budget if a much larger (ca. 2.1V)  $\Delta E$  is applied. Now, according to the standard potentials shown in Fig. 4 [ $-0.72V - (-1.33V) = 2.05V$ ],  $\Delta E$  is sufficient to simultaneously oxidize and reduce opposite sides of the film to the Os(III) and Os(I) states, respectively. Electroneutrality and the limited anion budget within the film are satisfied by migration of anions from the Os(I) side to the Os(III) side. The resulting concentration profiles of Os(III), Os(II), and Os(0) sites are diagrammed in Fig. 5B. The slopes of the concentration profiles are related to the magnitudes of  $D_{e(III/II)}$  and  $D_{e(II/I)}$ , and the populations of Os(III) and Os(I) sites are (to satisfy charge balance) equal. The limiting current for this measurement of electrical conduction across the poly-[Os] sandwich reflects the rate of electron self exchange chemistry in the absence of a bathing electrolyte solution and in some cases in the absence of solvent altogether. We believe this experimental capability may have significant fundamental and application utility.

Few examples of polymer sandwich electrodes have been studied so far, due, in part, to technical limitations in fabricating the microstructure. For instance, the mechanically formed type of sandwich used for poly-pyrrole is limited to relatively thick ca 10 $\mu$ m films and is furthermore not optimal for

counterion access to the film. The Au evaporation method used to make the poly-[OS(hpy)<sub>2</sub>(vpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> sandwich is useful for much thinner (0.1-0.5 $\mu$ m) films but is prone to shorting of the electrodes through minute pinholes in the polymer film (10). Such problems should be soluble, however, by adapting the reservoir of sophisticated microfabrication strategies accumulated in the microelectronics industry. "Opening up" the sandwich to the open face" format of an array electrode is one such strategy.

**Array Electrodes.** The simplest version of this very new microstructure arrangement consists of two closely spaced, parallel electrodes separated by an insulating gap (Fig. 2B). Layering an electroactive polymer film over electrodes and gap as diagrammed in Figure 2B gives an arrangement formally equivalent to an "open face" sandwich electrode. For polymer film thicknesses small compared to the gap, the interelectrode gap is equivalent to the sandwich electrode thickness and the thickness of the polymer film on the array times the length of the parallel electrodes is equivalent to sandwich electrode film area. The area can be large since the electrodes can be "folded" to form a pattern of interdigitated fingers called an interdigitated array (IDA).

The Wrighton group (29,30) recently described the first examples of array electrodes coated with electroactive polymers. They prepared arrays with eight independently addressable parallel Au film electrodes, each 140 $\mu$ m long and 3 $\mu$ m wide and separated from one another by insulating 1.4 $\mu$ m SiO<sub>2</sub> gaps. By independent control of the Au electrode potentials, poly-pyrrole coatings could be electropolymerized onto a single electrode, onto adjacent pairs, or over the entire array. Importantly, the poly-pyrrole could be made to cover the interelectrode gaps or not, as desired. For the case where two adjacent

disk microelectrode in Fig. 2C has an area of  $8 \times 10^{-7} \text{ cm}^2$ . A 100nm thick poly-[Os(bpy)<sub>2</sub>(vpv)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> coating on such an electrode contains only about 1,000,000 monomer sites, a tiny quantity in chemical terms (36). The currents which flow at the microelectrode are also tiny (down to pA), a simple fact which has opened to electrochemical experimentation, solvents with heretofore unusably low dielectric constants, like benzene (37), toluene and heptane (38). Such solvents can be profound effects on polymer coatings; electron and counterion mobilities in poly-[Ru(bpy)<sub>2</sub>(vpv)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> films are 10-100%, less for example, in toluene as compared to acetonitrile, indicating a stiffened polymer structure due to the tight ion pairing in toluene solvent (38). Microelectrode experiments clearly will be valuable in understanding the "dry" sandwich electrode experiments mentioned above.

Polymer coated microelectrodes also find usefulness as bio-sensors because of their small overall physical dimensions. Microelectrodes as a subject grew, in fact out of a search for in vivo electroanalytical probes in neurochemistry pioneered by the Ralph Adams group at Kansas. A glassy carbon electrode has for example been coated with Nafion polymer films in a successful scheme for dopamine neurotransmitter detection (39) in rat brain.

**Bilayer Electrodes.** The interface between two different, overlaid electroactive films can act as a chemical free energy based rectifying junction (17,40). The redox potentials of the polymers selected in designing a bilayer microstructure is crucial; those in Figure 2D, an electrode/polymer A/polymer B/electrolyte solution arrangement, are typical although others are possible and have significance.

The principles of bilayer electrodes are straightforward. Because polymer B is not in physical contact with the Pt electrode, the Pt electrode can

electrodes and intervening gap had been coated, the electrical conductivity of poly-pyrrole in the interelectrode gap was assessed as a function of oxidation state, with results similar to those in Fig. 4B.

The reports of the Wrighton group aptly preface the utility of array electrodes in constructing microstructures for both fundamental and device applications. An advantage over sandwich electrodes is that the sensitivity of the microstructure to polymer film pinholes and electrode shorting is transferred from the polymer-coating step to the array-fabrication step, which is based on relatively well understood microlithographic technology. This means that arrays may be applicable to a larger range of electroactive polymer types for investigation of the relation of conductivity to polymer oxidation state. Also, multiple electrodes can be used in varying geometries in the array, several polymer films can be applied to a single array, and ions and chemical reagents may have easier access to film structures designed as analytical sensors. The Wrighton group has already illustrated some of these points (31).

We have also been interested in array electrodes. Using a 3µm gap 1DA made with Pt film electrodes we have observed (32) the redox conduction of poly-[Os(bpy)<sub>2</sub>(vpv)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> polymers and DC electrogenerated chemiluminescence from solutions of the well-studied (32,34) complex [Ru(bpy)<sub>3</sub>]<sup>2+</sup>. It can be expected that as electrochemists become more familiar with the microlithography required to produce arrays, they will become a popular base for polymer microstructures. Whether the array electrode gap will surpass the 0.1µm gap dimension achievable with sandwich microstructures remains to be seen however.

The mere fact of shrinking the geometrical area of an microelectrodes. For example, the one-terminal, 10µm electrode has great consequences (35).

oxidize or reduce polymer B states only indirectly, via the  $E_{A1}^0$  and  $E_{A2}^0$  oxidizing and reducing states of polymer A respectively. Thus, a cyclical excursion of the Pt electrode potential from  $E_{Pt,1}$  to  $E_{Pt,2}$  and back first oxidizes polymer A and thereby polymer B, and then re-reduces polymer A, but does not re-reduce the film of polymer B. The current that oxidizes polymer B passes the polymer A/polymer B interface in a rectified manner, leaving polymer B charge trapped in its oxidized state. A secondary event is required to discharge (charge untrap) polymer B; this can occur via raising the electrode potential to  $E_{Pt,3}$  resulting in reduction of polymer B by the  $E_{A1}^0$  level of polymer A. Polymer B can alternatively be reduced via a photolytic reaction, by reaction with a solution component, or by a back reaction (thermodynamically unfavorable and thus slow) with the  $E_{A1}^0$  level.

The current and charge rectification properties of bilayer microstructures have many possible applications as discussed later. Bilayer electrodes also be used to probe the polymer film/film interface, by measuring the rate at which the monomolecular layer of polymer A sites at the film/film interface exchanges electrons with the opposite monolayer of B sites (41). The kinetics of such interfacial processes had never been previously explored. In a bilayer electrode with redox levels positioned as in Fig. 2E, so that the film/film electron transfer is thermodynamically unfavorable and slow (but not so slow as to be unobservable) and with the Pt electrode potential set so that the overall polymer B to electrode electron transfer is favorable, the film/film interfacial electron transfer can become the rate-determining step in bilayer charging. The polymer bilayer used (41) was  $Pt/poly-[Ru(vbpy)_3](ClO_4)_2/poly-[Os(bpy)_2(vpy)_2](ClO_4)_2$ , and the interfacial rate constant for the 405 mV

uphill reaction



was found to be within 30-fold of that predicted for the self-exchange rates of similar monomer complexes dissolved in solution. Reaction 4 is remarkably fast, given the many potential chemical and physical barriers that one could readily envision to exist at a polymer/polymer interface. This observation is encouraging for deriving fast switching times in bilayer electrode applications.

Successful functioning of bilayer electrodes depends upon making relatively pinhole-free polymer A films and upon no (or slow) intermingling of the two polymer A and B films. Bilayers are in fact fairly forgiving of an occasional pinhole, and many combinations (40) of different polymers have been made into bilayers with no detectable film/film intermixing effects at least on the scale of the film thickness.

Bilayer electrodes can be fashioned as sandwich (42) and array (43) electrodes, e.g., electrode/polymer A/polymer B/electrode, arrangements that are useful for electron diffusion studies as well as interesting electrical effects. Ion Gates. The ion gate (Fig. 2F) is a microstructure designed to control the flow of ions rather than of electrons (44,45). The electroactive polymer is coated on (around) a porous electrode to form a free-standing membrane which separates two electrolyte solutions. Its action rests in principle on how the permeability of the electroactive polymer to ion flow changes when, by control of the porous electrode potential, its oxidation state is changed.

The ion gate was illustrated (44) by coating a Au minigrad porous electrode with poly-pyrrole. Oxidized poly-pyrrole is poly-cationic and freely permeable to small anions, whereas poly-pyrrole is much less ionically

permeable (by  $\approx 10^2$ -fold). Thus, by manipulating the porous Au electrode potential, the flow of ions through the membrane could be reversibly and repeatedly, turned "on and off".

Like the other microstructures, the ion gate is useful for fundamental investigations, in this case for measuring the ionic conductivity of polypyrrole as a function of oxidation state (45,46) and showing that it parallels the electronic conductivity (Fig. 3B). The ionic conductivity measurement has practical significance as well, since polypyrrole is of interest for charge storage (battery) applications. The ionic conductivity of reduced polypyrrole is so poor that, unless a polypyrrole battery film is well designed to facilitate the in/out flow of counterions, severe ohmic voltage losses will occur during battery charge or discharge.

#### TOWARDS A MACROMOLECULAR ELECTRONICS

"Macromolecular electronics" is not yet a useable reality; this section is written in the spirit of setting out an overall conceptual framework for exploiting the electrical and ionic properties of electroactive polymer microstructures. For exploring new concepts that have as yet no current application, we make no apology, especially since we have already shown how developing the microstructures has had a significant payoff (up front) of basic knowledge about electron and ion transport in electroactive polymers. Also, while the polymer microstructures discussed here are based exclusively on electroactive materials, it is possible that the film making methods that are being developed will be of advantage in making thin, non-electroactive (insulating) polymer films useful in solid state electronics.

**Applications of Bilayer Electrode Rectification Effects. Charge Trapping.** In the bilayer electrode scheme of Fig. 2D, the oxidized form of polymer B can be

forward and trapped by changing the electrode potential from  $E_{Pt,1}$  to  $E_{Pt,2}$  and back. This trapped, oxidized state amounts to a charge memory (17,40) which can be "read out" by a subsequent potential excursion from  $E_{Pt,1}$  to  $E_{Pt,3}$  and back. The bilayer is further an accumulating charge memory, because within the redox capacity of polymer B charge may be summed up over many excursions from  $E_{Pt,1}$  to  $E_{Pt,2}$ . The essential difference between charge storage in a bilayer and in a conventional chemical battery is that the bilayer is an stably switched memory element; different potential excursions are necessary for memory input and output. This feature is implicit in all bilayers that have two, widely spaced redox levels  $E_{A1}^0$  and  $E_{A2}^0$  in the inner, polymer A, film as in Fig. 2D.

If polymer B has intense colorations that differ for its oxidized and reduced states, then the bilayer is a color memory as well as a charge memory (47). This characteristic may be useful in electrochromic displays, which are an active research topic which appears close to useable technology (48). The bilayer configuration would allow stable switching between the color of reduced and oxidized polymer B, an important addressing aid in the switching of a multiple element display. Stable switching of polymeric, electrochromic films can also be accomplished using the rectifying characteristics of a semiconductor electrode, as has been recently shown (49).

Alternatively, polymer B may react as a sensor of trace reductants or oxidants which diffuse to it from the contacting solution (perhaps a selective sensor by design of its chemistry). The charge stored on reduced or oxidized polymer B can be read out by either trapping or untrapping potential excursions, depending on the chemistry involved. Since the charge is stored cumulatively, great sensitivity is achievable, as illustrated (47) by detection

of dissolved adventitious oxygen at the  $\approx 10^{-6}$  M level.

Electron hole pair separation. If illumination of a bilayer electrode produces an excited state of polymer B that is capable of oxidizing polymer A, and the electrode potential is set so as to re-reduce the oxidized polymer A sites, a cathodic photocurrent will flow at the electrode. Oyama, et al (50) have demonstrated this important principle with a bilayer composed of a film of a Ru poly-pyridine complex covered with a film of a viologen polymer. Using the chemical free energy difference at a bilayer film/film interface in this manner is formally analogous to bandgap adsorption and electric field-driven electron-hole pair separation in a semiconductor space charge region (51). Bilayer electrode light harvesting efficiencies are likely to be less than those of semiconductors, however, unless polymers or modified microstructures can be identified which allow substantial exciton migration or the equivalent thereof, and where the ground state back electron transfer reactions are slow. Also, to prevent the film of polymer B from gradually becoming completely reduced, the contacting solution must contain a chemical oxidant, or a second electrode must be provided to act as an electron acceptor as in the sandwich or array electrodes. Oyama, et al (50) used dissolved  $O_2$  as the oxidant; the effect was to re-generate viologen (polymer B) and also partially quench the ground state back reaction of reduced viologen with the Ru(III) polymer.

#### Current-potential Characteristics and Amplification. Two Electrode Structures:

Electrochemical diodes. That the current flowing through the electroactive polymer film in a sandwich electrode or on an array varies with interelectrode potential in a non-linear fashion has been pointed out by both Wrighton's laboratory (30) and our own (42). Little current flows between the electrodes

unless their potential difference exceeds a certain value, whereupon a steep increase in current occurs, much like a Zener diode breakdown voltage.

The specifics of the electrochemical diode depend on several parameters, but particularly upon the choice of electroactive polymer. For instance, the voltage of the rapid current rise for a poly-[Os(bpy)<sub>2</sub>(vpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> sandwich electrode in electrolyte solution depends on the potentials of the two electrodes relative to some reference electrode (42), but when used in vacuum (28) current flow starts at a characteristic value near  $E_{3/2}^0 - E_{2/1}^0$ . In both media, the current does not increase indefinitely but reaches a plateau when the limiting concentration gradient conditions of Fig. 5A or 5B are attained. An electrochemical diode made from an array coated with poly-pyrrole (30) has a current-voltage characteristic more like a conventional

p-n junction diode but the initial voltage can be varied systematically by choice of the reference electrode potential. Use of poly-aniline, a different conducting polymer, on the array (31) produces an unusual diode pattern; following an initial voltage breakdown, the current limits and then, at a larger interelectrode voltage, returns to a small value. This novel diode characteristic occurs because the conductive form of poly-aniline can be made insulating by either further oxidizing or reducing it. Diodes can also be based on polymer bilayers incorporated into sandwich (42) or array (43) electrodes.

The range of different current-potential characteristics may ultimately lead to unique uses for electrochemical diodes based on microstructured polymers. It is unlikely, however, that these electrochemical diodes will compete with the switching speed of solid state devices. The intrinsically slow transport of electrons and ions required to "turn on" electrochemical

diodes may on the other hand, be considerably ameliorated if the electrochemical diode macromolecular dimensions can be shrunk to molecular ones, since this shortens the transport distances.

Electrochemical diodes can emit light if the oxidized and reduced members of two different redox couples, generated at opposite faces of a sandwich electrode (or adjacent electrodes in an array), react energetically enough to produce luminescing, excited state species. This principle has not yet been demonstrated using electroactive polymers, but Bard and coworkers (52) have described the solution analog using a variety of dissolved redox couples in a twin electrode thin layer cell.

Three Electrode Structures: Electrochemical transistors and triodes. These microstructures seek indirect control of the current flowing between two electrodes contacting an electroactive polymer, by the potential applied to a third electrode. Two different microstructures have been reported that accomplish this (29,42). One, labeled a "triode" (42), was based on the poly-[Os(bpy)<sub>2</sub>(vpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> sandwich electrode with an external reference electrode as the third electrode carrying the input signal. The other, labeled a "transistor" and reported by the Wrighton group (29), was designed upon a three electrode poly-pyrrole array in the scheme where  $\text{ooo}$  is the array electrode and  $\text{xxx}$  is polymer film



In this arrangement, the gate electrode, whose potential is controlled relative to a reference electrode in the contacting solution, is capable of generating a

band of poly-pyrrole of widely varying conductivity that is interposed between the source and drain electrodes. As a consequence, the current flowing between the source and drain electrodes under the impetus of a constant impressed potential is very sensitive to the applied gate electrode potential. The significant feature is that the effect of the gate potential is greatly amplified; a tiny charge flowing to the gate has a large impact on the drain current.

While practical application will require substantial advances, the Wrighton group's achieving (29) amplification by this arrangement is an important conceptual step towards a macromolecular electronics. Amplifying signals based on chemical events is difficult, and has usually been sought via catalytic reactions. Recognizing that the gate electrode above could be replaced or controlled by an analyte-sensing reaction (31), the amplification demonstrated in the Wrighton experiment is also an attractive concept for novel, sensitive analytical sensors based on polymer coated arrays.

Ionic Effects. Since the ion gate is a remotely, electrically switchable membrane, it offers an "on-off" avenue for control of ion transport from one medium to another. Ionic reagent release is one possible application and Miller and coworkers (53) have exploited this by soaking poly-pyrrole films in glutamate solutions, taking this anion into the films as a counterion. Then, reducing the poly-pyrrole film releases the glutamate into the contacting solution in small but controllable doses. In a microelectrode format, such a device could be valuable in neurochemical research.

In conclusion, we hope in this section to have impressed the reader not only with the primitive state of macromolecular electronics but also with the novelty of the concepts. The concepts in fact have on a number of occasions in

our own research outstrip the availability of suitable polymeric redox materials or our ability to fabricate a suitable microstructure from a polymer. A high priority in this field for those interested in practical applications will be development of a wide variety of robust, well behaved electroactive materials to be used in the microstructures. Given the fast pace of development of electroactive polymer films since the seminal reports of polymer film electroactivity (54-57), we are optimistic that many of the materials limitations will gradually be solved.

**Summary.** Electrochemically reactive polymers can be coated on electrodes in several microstructured formats called sandwich, bilayer, array, microelectrode, and ion gate electrodes. These microstructures can be used to study fundamental properties of electron and ion transport in the polymers and have potentially useful electrical responses.

#### **Acknowledgment.**

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### Figure Legends

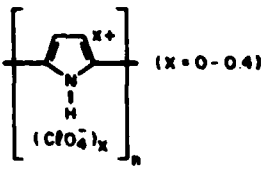
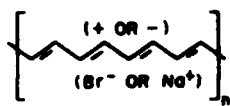
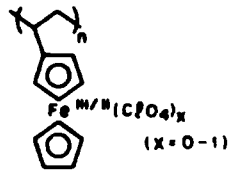
Fig. 1. Types of Electroactive Polymers. (see text for references).

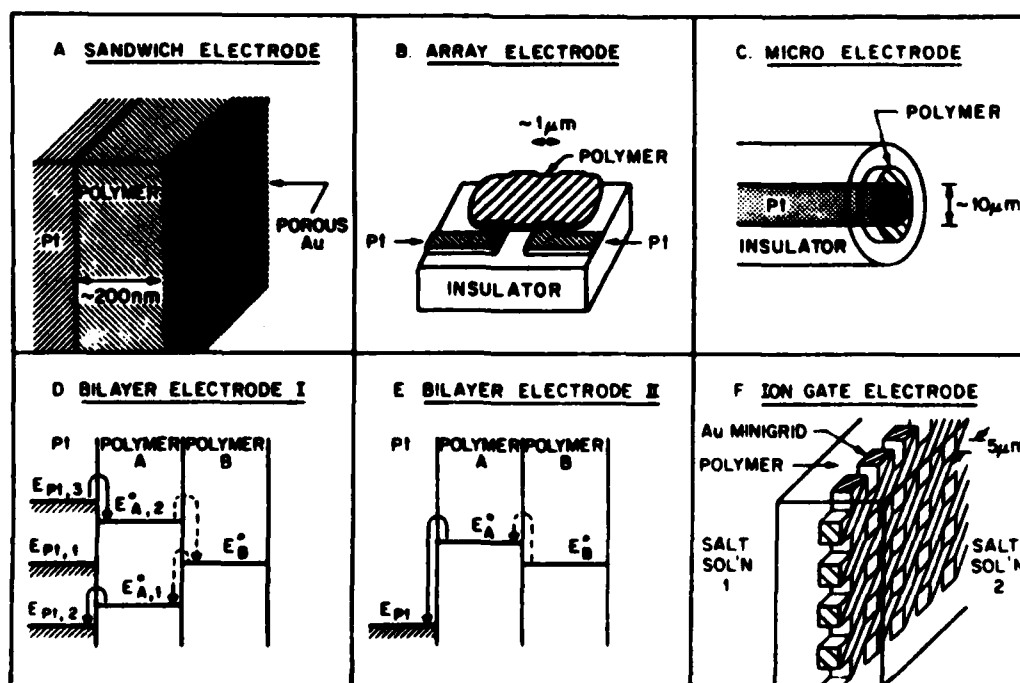
Fig. 2. Microstructures built from electroactive polymers. Except for A and B, which have been used dry, an electrolyte solution, reference electrode and counter electrode are typically present.

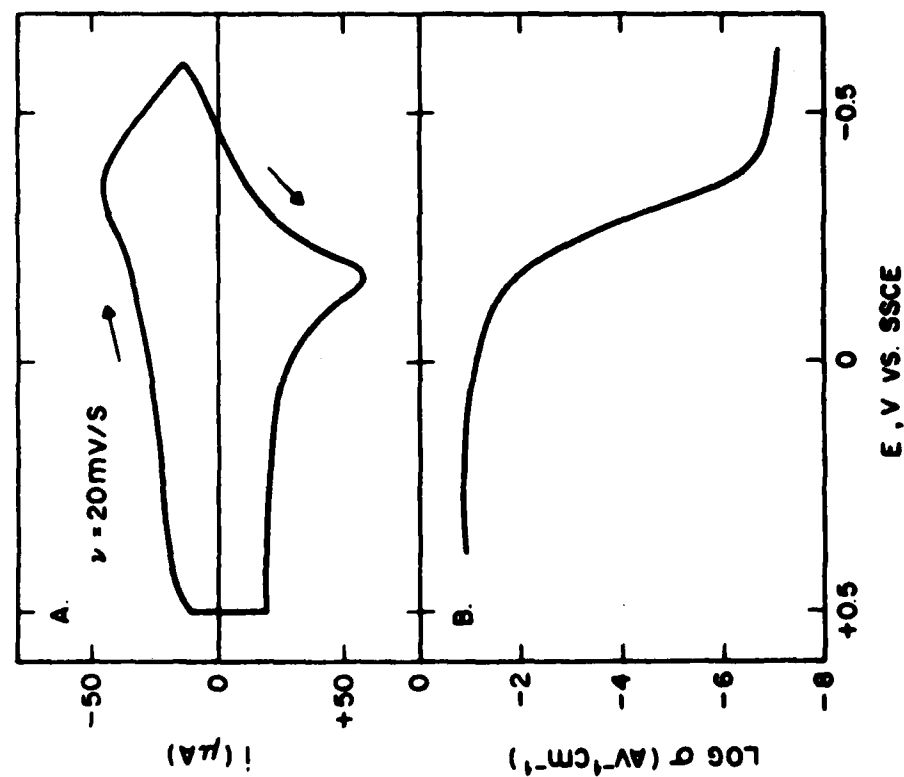
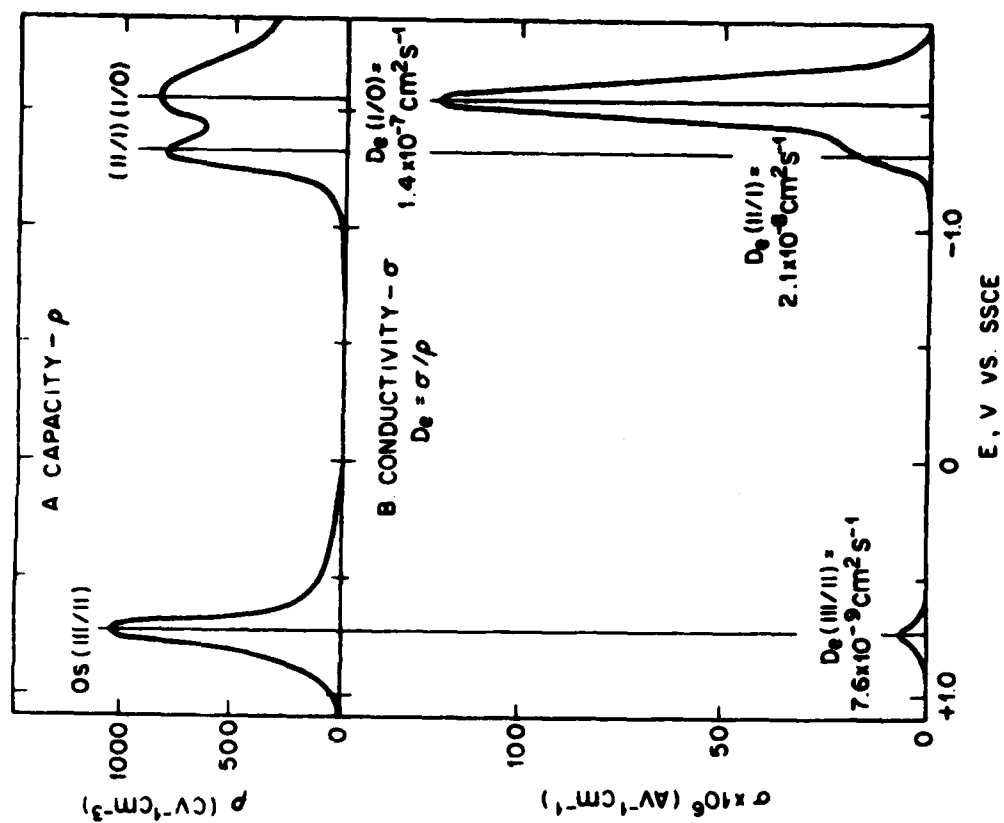
Fig. 3. A) Cyclic voltammogram and B) conductivity of poly-pyrrole film in contact with 0.1M Et<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN at room temperature.

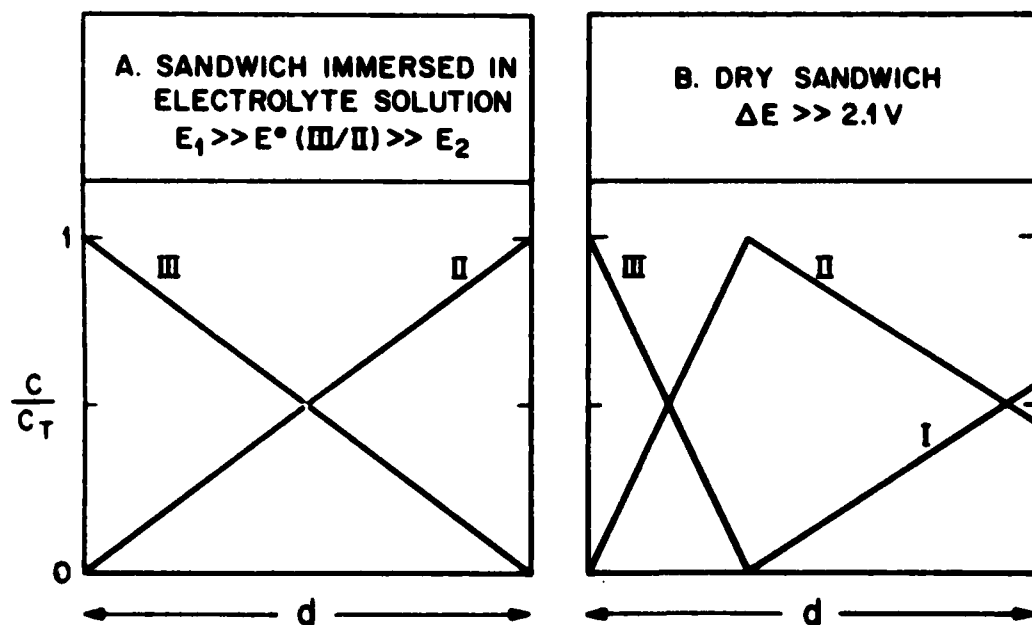
Fig. 4. A) Redox capacity and B) redox conductivity of poly-[Os(bpy)<sub>2</sub>(vpp)<sub>2</sub>](ClO<sub>4</sub>)<sub>n</sub> in contact with 0.1M Et<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN at room temperature.

Fig. 5. Concentration profiles of Os(III), Os(II) and Os(I) sites in A) a Pt/poly-[Os(bpy)<sub>2</sub>(vpp)<sub>2</sub>](ClO<sub>4</sub>)<sub>n</sub>/Au sandwich with  $\Delta E = 200$  mV centered about E° of the Os(III/II) couple, and B) a dry Pt/poly-[Os(bpy)<sub>2</sub>(vpp)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>/Au film with  $\Delta E > 2.1V$ .

TYPE	$\pi$ -CONJUGATED	COVALENT (NOT CONJUGATED)	ION-EXCHANGE
NATURE	"ELECTRONICALLY CONDUCTING": DELOCALIZED ELECTRONIC STATES DISTRIBUTED OVER A BROAD ENERGY RANGE	"ELECTRON-HOPPING": LOCALIZED REDOX COUPLES COVALENTLY BOUND TO POLYMER MATRIX (REDOX POLYMER)	REDOX ION DIFFUSION: MOBILE REDOX IONS HELD ELECTROSTATICALLY WITHIN POLYMER MATRIX
EXAMPLES	OXIDIZED POLY-PYRROLE  (x = 0-0.4)	POLY-[M(bpy)2(vpy)2(CF3SO3)x] (x = 0-3) M = Os, Ru bpy = 2,2'-BIPYRIDINE vpy = 4-VINYLPYRIDINE	Fe(CN)6 <sup>3-/4-</sup> IN PROTONATED POLY-(4-VINYLPYRIDINE)
	DOPED POLYACETYLENE  (Br <sup>-</sup> OR Na <sup>+</sup> )	POLY (VINYL FERROCENE)  (x = 0-1)	Co(bpy)3 <sup>3+/2+</sup> IN NAFION (A SULFONATED FLUOROCARBON POLYMER)







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